

# Geochemistry of the Floridan Aquifer System in Florida and in Parts of Georgia, South Carolina, and Alabama

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REGIONAL AQUIFER-SYSTEM ANALYSIS—FLORIDAN AQUIFER SYSTEM

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dosta and Brunswick, Ga., where large ground-water withdrawals have induced upward migration of highly mineralized water from deeper formations (Wait, 1965; Krause, 1979). Data from deep wells indicate that high  $\text{SO}_4^{2-}$  concentrations occur at depth in most of the study area except east-central and panhandle Florida. Thus, where the Upper Floridan aquifer is stressed by heavy pumpage, increases in  $\text{SO}_4^{2-}$  concentration may occur.

Bacterial reduction of sulfate probably occurs in all parts of the aquifer system; the importance of this process over the entire study area is difficult to determine owing to a lack of mineralogic and sulfur isotopic data. What is known is that bisulfide ( $\text{HS}^-$ ) is present over most of the region, but in highly variable concentrations (fig. 26). This variability in measured concentrations depends on several factors (Rye and others, 1981, p. 1943), such as (1) availability of organic material for sulfate reduction, (2) degree of confinement of the aquifer and loss of  $\text{H}_2\text{S}$  by diffusion, (3) availability of trace metals for reaction with the sulfide, and (4) loss of  $\text{H}_2\text{S}$  during sample collection or by inadequate sample preservation. The amount of  $\text{HS}^-$  measured in water samples might be only a fraction of the total sulfate reduction occurring in the Upper Floridan aquifer. It is possible that the trace amounts of dissolved iron in the system are sufficient over time to form iron sulfides (pyrite?) and consume most of the sulfide formed in the biochemical reaction. Plummer and others (1983, table 4) tested this hypothesis by assuming that the source of dissolved iron was the trace amounts of iron in carbonates; their mass-balance models showed that large amounts of sulfate could be reduced by methane oxidation with concurrent precipitation of pyrite. However, calculations of sulfur isotope balance indicated that such models were not feasible; the methane oxidation-pyrite formation models predicted values of  $\delta^{34}\text{S}_{\text{SO}_4}$  more than 20 ‰ heavier than was analyzed in water samples. The work of Plummer and others (1983) indicates that reduction of large amounts of sulfate and formation of large amounts of pyrite in the Upper Floridan are rather unlikely, especially since no enrichment of as much as 10 ‰  $\delta^{34}\text{S}_{\text{SO}_4}$  has been measured in water samples (table 17). The role of bacterial sulfate reduction in lowering  $\text{SO}_4^{2-}$  concentrations is probably limited to panhandle Florida, where gypsum is scarce and ground-water flow is sluggish. The low  $\text{SO}_4^{2-}$  concentrations mapped in southern Escambia and southwestern Santa Rosa Counties, Fla., occur in an area of high  $\text{Cl}^-$  concentrations, indicating that residual seawater is present in the aquifer system. Locally, the  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio is lower than expected from dilution of seawater, and high concentrations of  $\text{HCO}_3^-$  indicate that bacterial reduction of sulfate may be an important factor in lowering  $\text{SO}_4^{2-}$  concentrations.

#### DISSOLVED SOLIDS AND HYDROCHEMICAL FACIES

In water from the Upper Floridan aquifer, dissolved-solids concentrations vary from less than 25 mg/L near outcrops to more than 25,000 mg/L along the coasts. Within the system, the dominant cations are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  and the dominant anions are  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ . Locally, smaller amounts of dissolved iron, manganese, nitrate, phosphate, fluoride, strontium, sulfide, and silica also contribute to the dissolved-solids concentration. Generally, the dissolved-solids concentration of water from the Upper Floridan aquifer is less than 250 mg/L. In coastal areas, the Upper Floridan contains seawater, and fully penetrating wells may yield water with dissolved-solids concentrations approaching that of seawater, about 36,000 mg/L. Plate 8 shows the general distribution of dissolved-solids concentrations in water produced from wells that yield from the entire Upper Floridan aquifer. The map in plate 8 shows more mineralized water in inland areas than was shown in an earlier map by Shampine (1965b), because plate 8 was made using data from selected deep wells. In coastal and south-central Florida, very shallow wells in the Upper Floridan may produce water with concentrations of dissolved solids of less than 500 mg/L, but wells penetrating deeper than 100 ft will probably yield more mineralized water.

Generally, dissolved-solids concentrations in the Upper Floridan aquifer are maintained at less than 500 mg/L by saturation with calcite and dolomite, and by the limited presence of more soluble minerals such as gypsum; higher concentrations are generally due to the presence of seawater. High dissolved-solids concentrations along the coast of southeastern Georgia and northeastern Florida cannot entirely be attributed to seawater, however, because chloride concentrations in the Upper Floridan are not high. Extensive development of the Upper Floridan aquifer in this area has produced large head declines from predevelopment levels (Bush and Johnston, 1988, pl. 6). Declining heads apparently have induced water from the Lower Floridan aquifer to move upward or laterally, gradually increasing dissolved-solids concentrations over a large area. Recent studies of the effects of ground-water development in northeastern Florida (Fairchild and Bentley, 1977; Leve, 1983; Brown, 1984) indicate that water entering the Upper Floridan aquifer has increased the chloride concentrations in only a few wells as much as 50 mg/L, even though test wells indicate that water in the deepest parts of the Lower Floridan aquifer is a very saline, sodium-chloride type (Brown, 1980). Other data and studies cited in Brown (1984) indicate that highly mineralized, low-chloride water may have been present throughout most of the upper part of the Lower Floridan aquifer prior to devel-

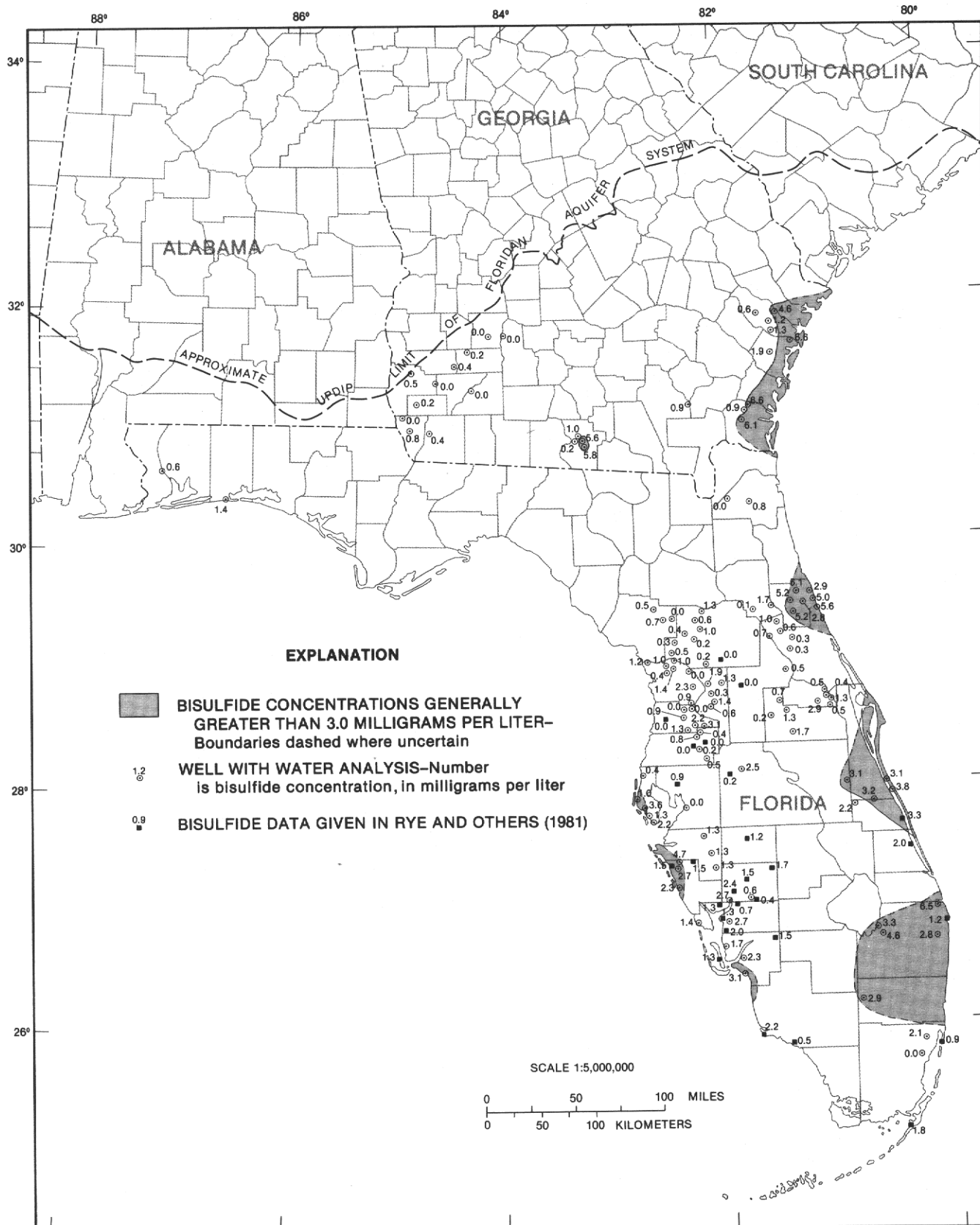


FIGURE 26.—Bisulfide concentrations in water samples from selected wells in the Upper Floridan aquifer.

opment. As heads declined, this low-chloride water began to move upward into the Upper Floridan aquifer. Recharge by highly mineralized, but initially low-chloride, water from the Lower Floridan appears to account for the increase in dissolved-solids concentrations in the Upper Floridan in this area.

Figure 27 shows the distribution of dissolved-solids concentrations in the Lower Floridan aquifer. This figure was prepared using both available chemical data and estimated heads in the system. There are few wells penetrating the Lower Floridan for which there are chemical data, and these wells do not generally penetrate the full thickness of the aquifer. Thus, figure 27 was made on the basis of the following assumptions: (1) data from fully penetrating wells should have more significance than data from shallower wells; (2) where the Lower Floridan merges with the Upper Floridan aquifer, dissolved-solids concentrations in the Lower Floridan are the same as concentrations in the Upper Floridan; and (3) chemical and hydraulic processes that control the chemistry of the Upper Floridan are also occurring in the Lower Floridan. As mentioned previously, heads in the Lower Floridan aquifer were assumed to be only 1 to 5 ft different from predevelopment heads in most areas of the Upper Floridan aquifer (Bush, 1982, p. 19). Where heads are high and fresh (low-chloride) water may be present to the base of the aquifer system (fig. 23), dissolved-solids concentrations should be controlled by the solubility of aquifer minerals. Because calcite and dolomite are at saturation in most of the Upper Floridan, these minerals were assumed to be at saturation throughout the Lower Floridan, and dissolution of gypsum (anhydrite) was assumed to have the greatest effect on dissolved-solids concentrations in low-chloride areas. Where estimated predevelopment heads are lower, both seawater and mineral dissolution will affect dissolved-solids concentrations. Although a hydrochemical facies map of the Lower Floridan could delineate areas where different geochemical processes are predominant, the data are insufficient to make such a map.

Areas where certain ions dominate the dissolved-solids content of ground water in the Upper Floridan aquifer are shown in plate 9. These dominant-ion patterns are called hydrochemical facies (Back, 1960, 1966). As stated by Back (1966, p. A1), "the facies reflect the response of chemical processes operating within the lithologic framework and also the pattern of flow of the [ground] water." Plate 9 was prepared by calculating and plotting the dominant cation(s) and anion(s) for all wells shown which had analyses of the major ions previously discussed. The area designated "Mixed" contains water with neither a single cation or anion constituting more than 50 percent of the total equivalence of cations or anions, nor any two

cations or anions constituting more than 75 percent of the total equivalence of cations or anions. The total cation or anion equivalence was calculated by dividing the concentration of each major cation or anion by its molecular weight, multiplying by its ionic charge, and adding the individual values (Hem, 1970, p. 82).

Study of the hydrochemical facies map suggests that there are four principal geochemical processes operating in the Upper Floridan aquifer:

1. Dissolution of aquifer minerals toward equilibrium as ground water moves from recharge to discharge areas,
  2. Mixing of fresh ground water with seawater in coastal areas, or with residual saline water where retained by low-permeability rocks,
  3. Mixing of ground water with recharge water, and
  4. Cation exchange between water and aquifer minerals.
- Each of these processes exhibits distinctive features on the hydrochemical facies map, as discussed below.

In most of Georgia and central Florida, mineral dissolution produces low to moderate increases in dissolved solids and diagnostic changes in dominant-ion chemistry. Ground water in the Upper Floridan aquifer in these areas is generally calcium-bicarbonate dominated, and dissolved-solids concentrations are generally less than 500 mg/L. Where dissolution of dolomite adds sufficient  $Mg^{2+}$  to the water, a calcium-magnesium-bicarbonate facies develops. Along the coast of Georgia and northern Florida, gypsum dissolution adds  $SO_4^{2-}$  and a calcium-magnesium-bicarbonate-sulfate facies develops. In southwestern Florida and in the Gulf Trough area of Georgia and Florida, gypsum is relatively abundant; sulfate is the predominant anion, and a calcium-magnesium-sulfate facies occurs.

Vertical mixing of freshwater and seawater occurs naturally in coastal areas along freshwater-saltwater transition zones. In these zones the water chemistry gradually changes from a calcium-magnesium-bicarbonate type with low dissolved solids near the top of the zone, to seawater at the bottom. Along the northwestern Gulf Coast of Florida the Upper Floridan aquifer is both highly permeable and unconfined; in this area the zone of transition is narrow (a relatively sharp interface occurs). Reichenbaugh (1972) presented data from Pasco County, Fla., indicating that the zone of transition is locally less than 200 ft thick. In contrast, along the east coast of central Florida the Upper Floridan aquifer is less permeable and is confined; no wells penetrate through the transition zone in this area, but available chloride data suggest that the zone is much thicker. Similar changes in hydrochemical facies occur along the coasts of central Florida and southeastern South Carolina because some seawater mixes with freshwater when a deep well is pumped. The small amounts of

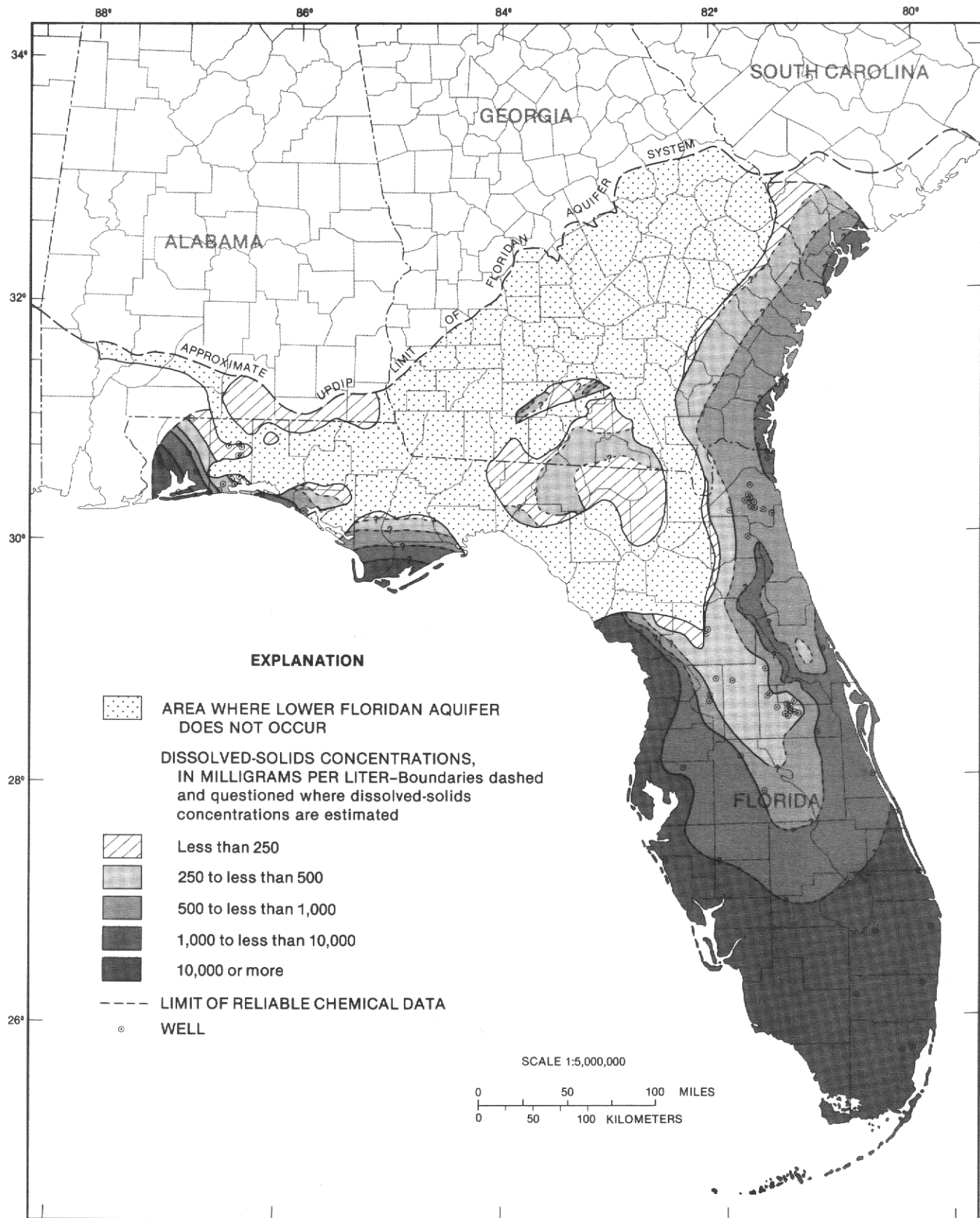


FIGURE 27.—Dissolved-solids concentrations in water from the Lower Floridan aquifer.

seawater, noted in samples from deep wells, are sufficient to change the water from calcium-magnesium-bicarbonate dominated to water with approximately equal proportions of all major constituents (designated "Mixed" in pl. 9). As the seawater content of the Upper Floridan aquifer increases, the dissolved-solids concentrations increase and there is a hydrochemical facies change to a sodium-chloride type of water. The effects of freshwater-saltwater mixing on samples from deep wells in coastal areas depend on the depth (position) of the transition zone, the depth of the well, and the pumping rate. Water from lightly pumped, shallow wells in most coastal areas should not be greatly affected by the seawater, and might be quite similar to freshwater from wells farther inland.

Mixing of ground water and residual saline water produces hydrochemical facies and dissolved-solids concentrations similar to those that result from mixing of ground water and modern-day seawater, except the facies occur in areas where a freshwater-saltwater transition zone in the Upper Floridan aquifer currently is not hydraulically possible. In south Florida, the aquifer system is extensively confined and residual saline water is present in the Upper Floridan. Tests in the Alligator Alley well in western Broward County (pl. 1) indicate that freshwater and saline water zones are intercalated (Meyer, in press b). Water samples from low-permeability zones in younger rocks contained  $\text{Cl}^-$  concentrations greater than those in samples from high-permeability zones in older (deeper) rock units. These results indicate that ground-water circulation in south Florida has been more effective in removing the residual saline water from the most permeable zones, not the shallowest zones, as one might expect. As mentioned previously, seawater probably entered the aquifer system along the St. Johns River valley during the Pleistocene (Stringfield, 1966) and has not been removed by the modern-day freshwater flow system. Mixing of this "residual seawater" with freshwater could produce the high dissolved-solids concentrations and sodium-chloride facies in this inland valley far from the sea.

An alternative explanation for the highly mineralized water in the Upper Floridan aquifer along the St. Johns River valley has been offered by Wyrick (1960) and Leve (1983). They suggest that deep saline water is rising into the Upper Floridan along fault zones in northeastern Florida, owing to higher heads occurring at depth. Invasion of the Upper Floridan aquifer by deeper, more mineralized water has been documented in Valdosta, Ga. (Krause, 1979), Brunswick, Ga. (Wait, 1965), and Nassau County, Fla. (Fairchild and Bentley, 1977). It is significant that each of these areas has high pumpage from the Upper Floridan. Only in the Brunswick area, however, has invasion of saline water caused higher dissolved

solids and a change to sodium-chloride facies in the Upper Floridan aquifer. The narrow band of calcium-magnesium-sulfate facies in northeastern Florida is apparently not related to mineral dissolution since the aquifer in this area is not gypsiferous. Upconing of mineralized water along fault zones may be the cause of this anomalous occurrence of sulfate dominance. Prior to development, the aquifer system was discharging to the St. Johns River, where the narrow band is mapped; the May 1980 potentiometric map (Johnston and others, 1981) indicates that the modern-day flow system is discharging to the river and to a pumping center on the south side of Jacksonville. These discharge patterns may have prevented the spread of the calcium-magnesium-sulfate facies eastward toward the coast.

Mixing recharge water with ground water causes variable chemical effects, depending on both the chemistry and the amount of recharge. Recharge from underlying sand aquifers in southwestern Georgia locally affects both  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations, but the quantity of recharge is not enough to change the predominant ions mapped in that area. Recharge through overlying sediments in the area immediately southeast of the Gulf Trough is more substantial (Krause and Randolph, 1989). This recharge is probably  $\text{Ca}^{2+}$ - $\text{HCO}_3^-$  type and is low in dissolved-solids concentration. The amount of recharge and the increase in ground-water circulation south of the trough affects dissolved-solids concentrations significantly. In the area of the trough, dissolved-solids concentrations are in the range of 250–500 mg/L, but through most of Leon County, Fla., and Thomas, Brooks, Cook, and Berrien Counties, Ga., concentrations are less than 250 mg/L. Also, the predominant ions change from calcium-magnesium-sulfate facies in the trough area to calcium-bicarbonate facies, typical of other recharge areas of the Upper Floridan. Recharge from underlying sand aquifers in east-central Georgia lowers  $\text{Ca}^{2+}$  concentrations and raises  $\text{Na}^+/\text{Cl}^-$  molar ratios but has no major effect on dissolved-solids concentrations or hydrochemical facies. Nearer the coast, in southeastern Georgia, a mixed-bicarbonate facies is mapped. In this area the Lower Floridan aquifer is probably discharging into the Upper Floridan, since this was a predevelopment discharge area for the Upper Floridan (fig. 12), and the cone of depression created by pumping near Savannah should further enhance upward discharge from the Lower Floridan. The chemistry of water in the Lower Floridan in the area is not known, but from the chemical changes noted in the Upper Floridan aquifer, estimates can be made. The water in the Lower Floridan must contain higher  $\text{Na}^+$  concentrations than the water in the Upper Floridan, since mixing tends to increase  $\text{Na}^+$  concentrations. Concentrations of  $\text{Ca}^{2+}$  in the Lower Floridan may be the same as or lower



than in the Upper Floridan; the effects of mixing on  $\text{Ca}^{2+}$  concentrations are not noticeable, and calcite is maintained at equilibrium. Simulation of the predevelopment flow system in this area indicates that small quantities of water flow from the Lower to the Upper Floridan aquifer (Krause, 1982); somewhat larger quantities may now be flowing because of development and pumpage from the Upper Floridan.

Ion exchange may be an alternative explanation for some of the patterns of hydrochemical facies discussed above. In east-central Georgia, the Upper Floridan aquifer is composed primarily of limestone, but even small quantities of clay minerals might be sufficient to exchange the required amounts of  $\text{Na}^+$  for  $\text{Ca}^{2+}$ . As with other geochemical questions unanswered in this report, detailed mineralogical studies are needed to test this hypothesis. Only in the western Florida Panhandle does ion exchange seem the most probable mechanism for developing the hydrochemical facies mapped in the Upper Floridan aquifer. In that area, the normal downgradient change from calcium-magnesium-bicarbonate to mixed facies does not occur. Rather, a mixed-bicarbonate facies evolves, which farther downgradient becomes a sodium-bicarbonate facies. There is a net loss of  $\text{Ca}^{2+}$  in the downgradient direction, which could result from calcite precipitation, as  $\text{HCO}_3^-$  concentrations are very high and calcite is at saturation. The source of additional  $\text{Na}^+$  is probably ion exchange because available chemical data indicate that mineral weathering is not a major source. Infiltration of  $\text{Na}^+$ -rich water is not possible since this is a discharge area for the Upper Floridan. Nor is upward leakage a plausible source, because, except in western Okaloosa County, Fla., the almost impermeable Bucatunna Formation separates the Upper and Lower Floridan aquifers. In addition, throughout most of Santa Rosa County, Fla., the Lower Floridan contains high  $\text{Cl}^-$  and dissolved-solids concentrations (figs. 24, 27), while concentrations of these constituents are low in the Upper Floridan, except in the vicinity of Pensacola Bay. Taken together, the chemical and hydrologic data indicate that ion exchange is the mechanism producing the sodium-bicarbonate facies that occur in the Upper Floridan aquifer in the western panhandle area.

#### MINOR CONSTITUENTS

##### FLUORIDE

The fluoride ( $\text{F}^-$ ) concentration in water in the Upper Floridan aquifer varies from nearly zero near outcrop areas to more than 4 mg/L in western Florida (fig. 28). Over most of the region, the  $\text{F}^-$  concentration is less than 1.0 mg/L, well within the mandatory standard (based on the annual average of maximum daily air

temperatures) of 1.4 to 1.8 mg/L for drinking water in the region (U.S. Environmental Protection Agency, 1975). In coastal areas, mixing of fresh ground water with seawater brings  $\text{F}^-$  concentrations to approximately 1.5 mg/L, depending on the depth of the well and the amount of seawater in the Upper Floridan aquifer.

Water recharging the aquifer system is the principal source of  $\text{F}^-$  in the freshwater parts of the system. In unconfined areas,  $\text{F}^-$  concentrations are very low, reflecting the low concentrations of  $\text{F}^-$  in rainfall: Irwin and Kirkland (1980) reported that  $\text{F}^-$  concentrations in rainfall at Maitland and Ocala, Fla., averaged 0.1 mg/L (range, 0.0 to 0.2 mg/L at Maitland and 0.0 to 0.3 mg/L at Ocala). Where the aquifer system is confined, recharge water contains  $\text{F}^-$  dissolved from carbonate fluorapatites, which are relatively abundant in the Miocene sediments of the system's upper confining unit. Once the  $\text{F}^-$  in recharge water enters the Upper Floridan aquifer, it appears to be chemically conservative. Fluorite ( $\text{CaF}_2$ ) is consistently undersaturated in water samples from the Upper Floridan and should not be controlling  $\text{F}^-$  concentrations. Fluoride-bearing apatites may control  $\text{F}^-$  concentrations, but these minerals form very slowly and are generally highly oversaturated in water samples from wells in the Upper Floridan aquifer (table 9, fig. 29). Anion exchange of  $\text{F}^-$  for hydroxyl ions ( $\text{OH}^-$ ) in apatite is well known (for example, Krauskopf, 1979, p. 74) and probably occurs to some degree in the Upper Floridan. The extent to which anion exchange removes  $\text{F}^-$  from ground water in the Upper Floridan aquifer cannot be determined at this time, owing to lack of data on the quantity and chemical composition of apatite in the aquifer.

It is difficult to prove with available data that equilibrium between ground water and a carbonate fluorapatite phase is (or is not) controlling  $\text{F}^-$  concentrations. The use of WATEQF to calculate the S.I. of various apatite species in water samples from the Upper Floridan aquifer is complicated by several factors: (1) phosphate concentrations were determined in Upper Floridan water samples that had passed through a relatively coarse filter (0.45 micrometer ( $\mu\text{m}$ )), thus allowing whole microorganisms or parts of microorganisms to be analyzed along with "dissolved" phosphate (see later section on "Nutrients"); (2) apatites in nature occur as a solid-solution series containing variable amounts of calcium, sodium, magnesium, strontium, phosphate, carbonate, sulfate, and hydroxide (McClellan and Lehr, 1969; Baturin and others, 1970; McArthur, 1978; Manheim and others, 1980; Gulbrandsen and others, 1984), and each species has a different solubility in ground water (Brown, 1960; Roberson, 1966; Wier and others, 1971; Chien and Black, 1976; Nathan and Sass, 1981); and (3) the composition of apatites in the Floridan aquifer system is not